(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 April 2001 (05.04.2001)

PCT

(10) International Publication Number
WO 01/23883 A1

(51) International Patent Classification[7]: G01N 33/00, 33/34, 1/00, 33/02, 33/14

(21) International Application Number: PCT/GB00/03664

(22) International Filing Date: 25 September 2000 (25.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9922642.5 25 September 1999 (25.09.1999) GB

(71) Applicant *(for all designated States except US)*: QUALITY SENSOR SYSTEMS LTD. [GB/GB]; Greenfield Business Centre, Greenfield, Flintshire CH8 7GR (GB).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: FARRINGTON, Amiel [GB/GB]; 7 Croft Close, Utkinton, Tarporley CW6 0XA (GB).

(74) Agent: STUTTARD, Garry, Philip; Urquhart-Dykes & Lord, Tower House, Merrion Way, Leeds LS2 8PA (GB).

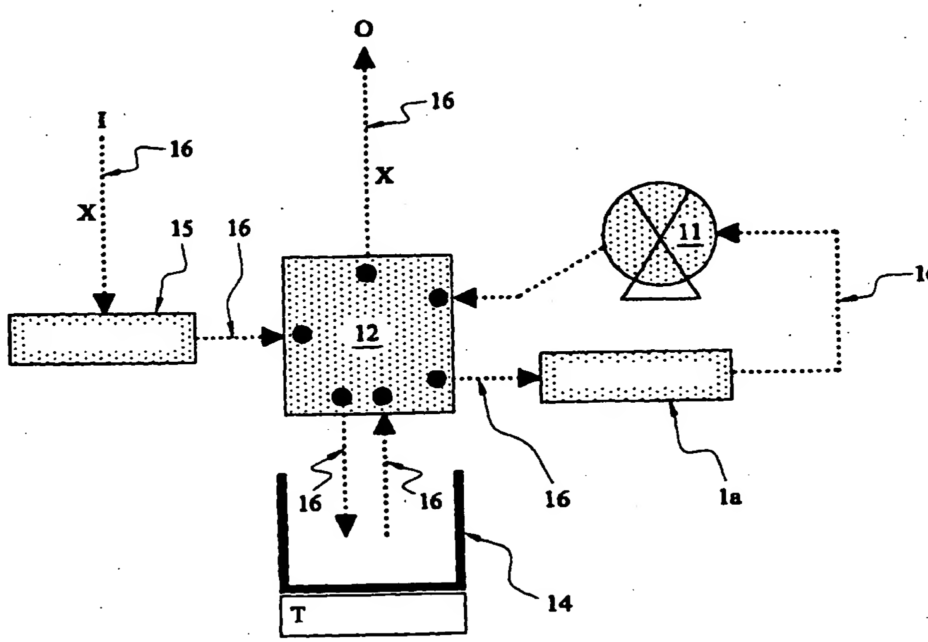
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CHEMICAL SENSING SYSTEM



(57) Abstract: A chemical sensing system for gas or vapour analysis of a sample of interest, in particular to an array-based chemical sensing system for gas or vapour headspace analysis of food packaging materials.

WO 01/23883 A1

CHEMICAL SENSING SYSTEM

The present invention relates to a chemical sensing system for gas or vapour analysis of a sample of interest, in particular to an array-based chemical sensing system for gas or vapour headspace analysis of food contact packaging materials.

Current legislation requires that materials and articles that come into contact with food must not transfer their constituent chemicals to the food in quantities that would either endanger health or cause the food to become tainted or odorous. By way of example, chemicals which cause packaging to become tainted or odorous packaging may migrate into the food placed within the packaging. Food products such as chocolate and tea are particularly sensitive to taint and odour. Manufacturers of food contact packaging are therefore required to undertake "taint and odour" testing in order to observe stringent quality control procedures defined by current legislation and to meet the requirements of their customers.

Although the analytical chemist has available to him an extensive range of conventional instrumentation, quality control techniques are generally confined to the remote laboratory under the direction of trained personnel. Currently food contact packaging manufacturers rely in general on human sensor panels (HSPs) and/or gas chromatography/mass spectrometry (GC/MS) for quality control. HSPs have remained the industry standard for "taint and odour" testing for over two decades but suffer from two major disadvantages: (1) HSPs are subjective and cannot be calibrated against other panels (and are therefore prone to

error) and (2) HSPs are an off-line technique providing results 36 hours or more post production. Whilst being an accepted analytical technique, GC/MS remains a remote procedure and GC/MS devices are expensive to install and run and are operable only by trained operators.

There is an increasing demand to improve quality control procedures and to reduce the costs attributable to production mistakes. Bringing quality control techniques to the factory floor using technology for non-skilled operators is an extremely important goal to many manufacturing industries. For example, if an analytical technique is to provide added value to a carton manufacturer's quality control procedures, it should be able to provide reliable quality control information in a production environment.

The present invention seeks to fulfil the demand for improvements in quality control by providing an array based chemical sensing system. More particularly, the present invention provides a chemical sensing system comprising a modular sampling unit adapted such that the majority of the surface area of a sample (*eg* a paperboard carton or related raw material) is exposed to a continuous flow of a carrier gas (*eg* air) whilst minimising the sampling dead volume operatively connected to an array based chemical sensor assembly which exhibits improved sensitivity. Whilst there is little or no sample preparation before use, the chemical sensing system is able to provide rapid results at-line rather than post-production.

Thus viewed from one aspect the present invention provides a chemical sensing system for analysing the

headspace of a sample comprising a modular sampling unit operatively connected to a chemical sensor assembly, wherein:

(1) said modular sampling unit comprises:

a mount having an inlet channel and an outlet channel for a carrier gas;

a base member having a hollow interior bound by one or more internal side walls and a basal wall, wherein at least a part of the juncture of the basal wall and one or more internal walls is provided with a supporting collar for supporting the whole or part of the edge of the lower face of the sample;

a closure member having one or more exterior side walls and a basal wall defining a body portion, said body portion being complimentarily shaped with the hollow interior of the base member, wherein the outer edge of the basal wall is provided with an upstanding portion capable of engaging the edge of the upper face of the sample,

wherein in use the base member is inserted into the mount and the body portion of the closure member engages the hollow interior of the base member thereby defining a headspace below the lower face of the sample and a headspace above the upper face of the sample such that the inlet channel communicates with the headspace below the lower (or with the headspace above the upper) face of the sample and the outlet channel communicates with the headspace above the upper (or with the headspace below the lower) face of the sample thereby defining a continuous flow path between the inlet and outlet channel across the majority of the surface area of the sample; and

(2) said chemical sensor assembly comprises:

one or more chemical sensors, each chemical sensor having a chemical sensing component capable of exhibiting a

measurable and characteristic response to a chemical stimulus;

a solid body having an entry end for admitting a carrier gas, an exit end for exhausting a carrier gas and one or more compartments for housing each of the one or more chemical sensors therebetween, said one or more compartments being in consecutive fluid communication so as to define a continuous flow path between the entry end and the exit end of the solid body in which the chemical sensing component of the or each chemical sensor may be exposed to the carrier gas.

In use, a carrier gas is introduced into the inlet channel of the modular sampling unit where it sweeps the headspace of the sample. The carrier gas (containing one or more chemical stimuli from the headspace) is then drawn over each chemical sensor in the array and interacts to varying extents with each chemical sensor to yield a time dependent response profile which is characteristic of the chemical stimuli. Statistical methods for defining X% confidence intervals on multi-variate sample populations in conjunction with data reduction techniques may be used to draw conclusions as to the identity of the unknown chemical stimulus. The analytical results may be obtained as simple or as complex as desired (*ie* a simple pass/fail answer with or without a certainty value or conclusions may be drawn as to the possible identity of the chemical stimuli).

In a preferred embodiment, the hollow interior of the base member and the body portion of the closure member are substantially cylindrical. In this embodiment, the supporting collar and/or the upstanding portion are substantially annular. The annular supporting collar may

contain one or more cut-away portions. The annular upstanding portion may be a solid ring.

In a preferred embodiment, the inlet channel is connected to the headspace below the lower face of the sample by a basal conduit in the basal wall of the base member. The base member is inserted into the mount such that the inlet channel and basal conduit are in fluid communication.

In a preferred embodiment, the outlet channel is connected to the headspace above the upper face of the sample by a side conduit in the side wall of the base member. The base member is inserted into the mount such that the outlet channel and side conduit are in fluid communication. Particularly preferably the headspace above the upper face of the sample and side conduit are connected in fluid communication by a linear tube disposed radially in the upstanding portion of the closure member. The upstanding portion may contain more than one linear tube to accommodate samples of varying thickness by allowing the extent to which the body portion of the closure member operatively engages the hollow interior of the base member to be varied.

In a preferred embodiment, the headspace below the lower face of the sample is in fluid communication with the headspace above the upper face of the sample via one or more substantially U-shaped tubes. Particularly preferably a first arm of the (or each) U-shaped tube is disposed radially in the supporting collar of the base member and a second arm of the or each U-shaped tube is disposed radially in the upstanding portion of the closure member, the first and second arm being connected in fluid communication by a

connecting portion in the side wall of the base member. The supporting collar of the base member may contain more than one first arm and the side wall may contain more than one connecting portion so as to accommodate samples of varying thickness by allowing the extent to which the body portion of the closure member operatively engages the hollow interior of the base member to be varied.

In a preferred embodiment, the basal wall of the base member comprises a protrusion for supporting the lower face of the sample. Preferably the protrusion is capable of supporting the substantially central region of the lower face of the sample. Preferably the protrusion converges to a reduced contact end (*eg* to a point) so as to maximise exposure of the lower face of the sample to the carrier gas. Preferably the protrusion is substantially cone-shaped.

In a preferred embodiment, the basal wall of the closure member comprises a protrusion for assisting sample location and retention. Preferably the protrusion converges to a reduced contact end (*eg* to a point) so as to maximise exposure of the upper face of the sample to the carrier gas. Preferably the protrusion is substantially cone-shaped.

Preferably the body portion of the closure member is threadedly engaged within the hollow interior of the base member. Preferably the base member is a tight push fit into the mount.

Preferably the exterior face of the basal wall of the base member and the mount comprise a locating arrangement to enable correct positioning and insertion of the base member in the mount. For example, the locating arrangement may

comprise a locating pin on the mount capable of cooperating with a locating aperture on the exterior face of the basal wall of the base member.

Preferably the inlet and outlet channels are sealingly isolated (*eg* using one or more O-ring seals in the mount). Preferably the inlet channel is sealingly isolated from the environment (*eg* using one or more O-ring seals in the mount). Preferably the outlet channel is sealingly isolated from the environment (*eg* using one or more O-ring seals in the mount). Preferably the headspace of the sample and the environment are sealingly isolated (*eg* using one or more O-ring seals in the closure member).

The sampling chamber defined when the base member is inserted into the mount and the body portion of the closure member engages the hollow interior of the base member may be tailored to conform to the characteristics of the desired sample (*eg* solid), to the sample size and/or shape and to considerations such as destructive or non-destructive sampling. Preferably, the sampling unit is adapted to define a sampling chamber for use with solid samples.

Preferably each compartment of the solid body is arranged such that the chemical sensing component is exposed to the carrier gas (containing the chemical stimuli from the headsapce) in a wall jet fashion. The "wall-jet effect" is generally known from the art of liquid dynamics where studies have been made on the effects of liquid impingement on an extended solid surface.

In a preferred embodiment, the entry end for admitting a carrier gas and the exit end for exhausting a carrier gas

are connected by a substantially linear conduit. Preferably the substantially linear conduit defines a spine connecting each of the compartments consecutively. Particularly preferably each compartment is connected in parallel spaced apart relationship. Particularly preferably each compartment is substantially perpendicular to the spine. Particularly preferably each of the compartments is symmetrically arranged around the spine. In this manner, the carrier gas passes into each compartment where it impinges on the chemical sensing component in a wall-jet fashion (*ie* a divergent flow path is created in each compartment causing the carrier gas to traverse the surface area of the chemical sensing component) in a repeatable manner.

In a preferred embodiment, each compartment is adapted to house the chemical sensing component in substantially free space. In this embodiment, the chamber is sized and configured in accordance with the size and shape of the chemical sensing component and to minimise the dead volume.

Preferably the chemical sensor assembly comprises a plurality of chemical sensors (*ie* an array). Array based sensing systems have been the subject of much research over the last fifteen years (see for example Gardner *et al*, Sensors and Actuators B, 1994, 18 to 19, 211; and Grate *et al*, Anal. Chem., 1988, 60, 2801) and their properties are in general familiar to those skilled in the art.

Preferably the chemical sensing component is a planar chemical sensing component. The planar chemical sensing component may be any convenient shape and of any convenient type as desired for the stimulus of interest. For example, each chemical sensing component may be of a bulk or surface

acoustic wave type, a metal oxide type, a conducting polymer type or an optical type. Such chemical sensing components are widely reported and well-known (*eg* optical sensor components in WO-A-98/22807). Preferred are quartz crystal chemical sensors (*ie* a bulk acoustic wave type sensor).

Generally but not essentially, one or both faces of the planar chemical sensing component is coated with a material capable of exhibiting or inducing a measuring response to the stimulus of interest. Materials and methods for coating sensor components are familiar to those skilled in the art and are widely reported such as in for example King, Anal Chem, 1964, 36, 1735.

The materials of the chemical sensor assembly are adapted to resist absorption of the carrier gas and to minimise cross-contamination. For example, the solid body is conveniently constructed of an inert material (such as PTFE). The chemical sensor assembly may be directly mounted on the electronic circuitry board. This has the added advantage that leads between the sensing assembly and electronic circuitry are eliminated so that sensitivity (*ie* signal to noise ratio) is enhanced.

The chemical sensor assembly is itself novel and improves the sensitivity of gas and vapour analysis by more effectively exposing chemical sensors to a carrier gas.

Viewed from a further aspect the present invention provides a chemical sensor assembly as hereinbefore defined.

The modular sampling unit is itself novel and improves the sampling operation by exposing the majority of the

surface area of a sample to a substantially uninterrupted flow of carrier gas (*eg* air) in a low dead volume. The advantage of this is that the concentration of the stimulus of interest in the carrier gas is optimised thereby enhancing overall sensitivity.

Viewed from a yet further aspect the present invention provides a modular sampling unit as hereinbefore defined.

The chemical sensing system of the invention is suitable for use in any application where gas or vapour phase analysis of a sample is desirable. For example, the invention may be used to screen for volatile components in food contact packaging (*eg* printed paperboard cartons, paper or related materials) or in textiles. For this purpose, the chemical sensing system preferably comprises a template for tailoring the sample to the size and configuration of the sampling unit.

Viewed from a yet still further aspect the present invention provides a method for detecting the presence of one or more chemical stimuli in the headspace of food packaging material using a chemical sensing system as hereinbefore defined, said method comprising:

inserting the base member into the mount;

positioning a sample of the food packaging material in the hollow interior of the base member such that the sample is supported on the supporting collar;

engaging the body portion of the closure member with the hollow interior of the base member;

sweeping the headspace of the sample with a carrier gas;

passing the carrier gas containing one or more chemical stimuli from the headspace to the entry end of the chemical sensor assembly;

measuring the response of the chemical sensors to the carrier gas containing the one or more chemical stimuli from the headspace; and

relating the response to the presence of one or more chemical stimuli.

The chemical stimulus of interest may be (for example) diisopropylnaphthalenes (DIPNs) and the method may be used to rapidly detect DIPNs in paperboard at the levels of current concern to the industry.

The chemical stimulus of interest may be (for example) hexanal and the method may be used to rapidly detect hexanal contained in paperboard at levels which are indicative of potential problems for food packaging.

The chemical sensing system of the invention and its component parts may be controlled using suitable expert software. The expert software may be adapted to control the process and analyse data instantaneously to permit use by non-technical operators. Equally, the chemical sensing system may support auto-checking procedures to track chemical sensors and components reliably and to implement calibration of the chemical sensor component.

The present invention will now be described in a non-limitative sense with reference to the accompanying Figures in which:

Figure 1 illustrates a cross-sectional view of an array based chemical sensor assembly of the invention;

Figure 2 illustrates in detail an individual sensor of the array based chemical sensor assembly shown in Figure 1;

Figure 3 illustrates a side view of an array based chemical sensor assembly of the invention;

Figure 4 illustrates schematically the control system of an array based chemical sensor assembly of the invention;

Figure 5 illustrates schematically the control system of an embodiment of the modular sampling unit of the invention;

Figure 6 illustrates schematically the gas flow through an embodiment of the chemical sensing system of the invention;

Figure 7 illustrates (a) the mount, (b) the base member and (c) the closure member of a disassembled embodiment of the modular sampling unit of the invention;

Figure 7d illustrates an assembled embodiment of the modular sampling unit of the invention; and

Figures 8 and 9 illustrate the results of test Examples of an embodiment of the chemical sensing system of the invention.

Figure 1 illustrates in cross-sectional view an embodiment of a chemical sensor assembly of the invention designated generally by reference numeral 1. The chemical sensor assembly comprises an array of eight individual quartz crystal gas sensors 2 for bulk acoustic wave sensing, each sensor 2 having a planar chemical sensing component 2a. Each sensor 2 is housed in one of a series of compartments 50 of a solid sensor block 1a made of an inert material such as PTFE. The sensor block 1a has a linear conduit 51 between entry and exit ends which interconnects the series of compartments 50 in parallel spaced apart relationship thereby defining a carrier gas flow path X in which each

planar chemical sensing component 2a is disposed so as to permit gas flow over its surface in a unique manner (see Figure 2).

Figure 2 illustrates in detail the flow path X of a carrier gas over the surface of the planar chemical sensing component 2a of the quartz crystal sensor 2. "Wall jet" impingement onto the chemical sensing component 2a leads to a divergent flow path around and over its entire surface thereby contributing to an overall improvement in sensitivity.

Figure 3 illustrates in side view the sensor block 1a connected directly to the electronic circuitry 3 (the combined unit being referred to as a sensor board 4).

The sensor board 4 is controlled by a microcontroller 6 (see Figure 4) which takes instructions directly from a personal computer C down an RS232 line 9. The microcontroller 6 controls each sensor transducer 5, drive and output, and the temperature of the sensor block using a feedback mechanism 7, 8. The temperature control 7 permits heating and cooling of the sensor block.

As illustrated in Figure 5, a control board 10 for a sampling unit 14 is controlled by a microcontroller 13 from a personal computer C taking instructions down an RS232 line 9. Commands may be issued from the personal computer C to the microcontroller 13 during use or using whole sampling routines which are downloaded and subsequently executed. The control board 10 controls the switching of a pump 11 and a series of valves 12 and the temperature of the sampling chamber 14. The control board 10 may also support a series

of LEDs or an LCD panel to indicate the status of the instrument.

With reference to Figure 6, during use a carrier gas such as air (or a vapour) is drawn along flow path X from an inlet I to an exhaust O via the sampling unit 14 and the sensor block 1a. Flow is achieved by virtue of a pump 11 and a series of valves 12 together with connecting pipework 16. The valves 12 and pump 11 are controlled by a microcontroller 13 (see Figure 5) which allows the carrier gas or vapour to be directed around the system and allows filtered air to be drawn through filter 15 and over the chemical sensors after use for the purposes of cleaning. The wetted material of the pump 11, series of valves 12 and connecting pipework 16 are chemically inert. The sampling unit 14 is provided with temperature control T.

Figures 7a, b and c illustrate a cross-sectional view of the disassembled components of a modular sampling unit of the invention. Figure 7a shows a mount 17 into which the base member of the sampling unit is engaged by a push-fit (described hereinafter). Channels 18a partially define the flow path X of a carrier gas. Correct location of the mount 17 with the base member of the sampling unit is aided by a locating pin 20. The gas tight seal between the mount 17 and the base member and the separation of the gas inlet and gas outlets is achieved by three O-rings 19.

With reference to Figure 7b, a base member 21 comprises a locating pin hole 22 which engages the locating pin 20 of the mount 17 into which the sampling base 21 is inserted by a push-fit. A sample (for example paperboard) is cut to a predetermined size using a template and is placed into the

base member 21 where it is supported on internal walls 24a. Channels 18b align with channels 18a of the mount 17.

Illustrated in Figure 7c is the closure member 25. The closure member 25 is secured to the base member 21 by means of a screw thread 23b on the body portion 54 engaging an internal thread 23a on the base member. An O-ring 26 provides a gas tight seal between the base member 21 and the closure member 25. The basal wall of the closure member 25 comprises upstanding portions 24b which engage the uppermost surface of the sample.

Each of the base member 21 and closure member 25 are manufactured from inert materials and/or from materials which enable the chamber to be disposable or alternatively which allow cleaning and re-use.

Figure 7d shows a fully assembled modular sampling unit of the invention in which the base member 21 is inserted in the mount 17 and the closure member 25 is screwed into the base member 21. The sample is supported on internal walls 24a of the base member and the upper surface is sealingly engaged by upstanding portions 24b. A U-shaped tube 56 is formed during assembly to complete the continuous path X for flow of carrier gas across the majority of the exposed surface area of the sample. In this manner, a carrier gas may be used to sweep the headspace of the sample in an effectively low dead volume.

Example 1 - **Demonstration of "at-line" Analysis**

Experimental

Various carton samples of a single production run were analysed using an embodiment of a chemical sensing system according to the invention. Samples were taken at different post-production times (including immediately post-production, at 14 hours post-production and at numerous intervals therein). 50 x 60 mm squares were cut from the board and no further sample preparation was undertaken.

Results

The combined chemical sensor responses to replicate carton samples of a duplicate production run were used to define a qualitative calibration. The "calibration" cartons had been previously certified to be "within specification" using an alterative analytical technique. The various production carton samples were compared to this calibration.

Table 1

Sample	Probability (%)	Status	Comments
0 hrs / 1	0.12	Reject	Immediate
0 hrs / 3	3.4	Reject	5 mins post-prod
0 hrs / 5	9.8	Accept	10 mins post-prod
0 hrs / 6	29.9	Accept	12 mins post-prod
4 hrs	21.6	Accept	Post-air
14 hrs	39.6	Accept	Current anal. time

Discussion

The carton samples that were taken straight from the press (0 hrs/1-6) demonstrate a gradual increase in certainty of belonging to the "standard" population. Whilst

sample 0 hrs/1 which was analysed immediately, is rejected from the "standard" population, sample 0 hrs/5 analysed 10 minutes post-production, is accepted as belonging to the "standard" population. This is almost certainly due to the rapid loss of residual solvents from the carton.

Conclusions

These results demonstrate that cartons could be analysed almost immediately post-production thus eliminating the current 14 hour "airing" period and 24 hour incubation period before carton samples can be checked for quality. In addition, production can be monitored during progress thus yielding added value to the manufacturer's quality procedures.

__Example 2__ - The Detection of hexanal in Paperboard

The presence of hexanal in raw paperboard is often perceived to be a marker of potential quality problems in the resulting packaging.

Experimental

Two samples of paperboard packaging were analysed using an embodiment of the chemical sensing system according to the invention. One sample was of "acceptable" packaging, the other had been "rejected" by a HSP. 50 x 60 mm squares were cut from the packaging and no further sample preparation was undertaken.

Results

The combined chemical sensor responses to replicate samples of the "acceptable" packaging were used to define a qualitative calibration. This calibration was used to compare the "rejected" packaging (Figure 8).

Discussion

Figure 8 demonstrates that the embodiment of the chemical sensing system according to the invention is clearly able to resolve low levels (< 0.8 ppm) from higher levels (1.6 ppm) of hexanal contained in paperboard. The levels of hexanal contained in the paperboard were independently determined using a traditional analytical technique. Investigations into other contaminants found in paperboard have demonstrated that the embodiment of the chemical sensing system according to the invention is able to provide reliable quantitative information over wide dynamic ranges.

Conclusions

The embodiment of the chemical sensing system according to the invention provides a rapid (< 2 minutes) technique to determine the hexanal content of paperboard which is of utility to both paperboard producers and to packaging manufacturers.

<u>Example 3</u> - The Detection of a Contaminated Food Contact Carton

Experimental

A "tainted" food contact carton sample was analysed using an embodiment of the chemical sensing system according to the invention. Samples of various cartons that were "in specification" were also analysed using the embodiment of the chemical sensing system according to the invention to provide the instrument calibration. 50 x 60 mm squares were cut from the board and no further sample preparation was undertaken.

Results

The combined chemical sensor responses to the "in specification" carton samples were used to define a qualitative calibration. The "tainted" food contact carton was compared to this calibration and the results are given in Table 2.

Table 2

Sample Name	Probability (%)	Status	Comments
T	0	Reject	Tainted carton
U	0	Reject	paperboard layer
V	7.1	Accept	Print layer of T

Discussion

The results of the sample comparisons to the "standards" calibration are presented as percentage probabilities of belonging to the "standards" population. The customary 5% significance level was applied as the pass/ fail boundary. The results identified the "tainted" carton

(T) as contaminated. This carton (T) had previously been analysed using a HSP and had "passed". It was later identified by a second HSP as being "tainted". This conflict of results draws attention to the subjective nature of the HSP technique. The "tainted" carton (T) was divided into its two component layers and re-analysed. The results suggested that the source of taint arose from the paperboard (sample U). The chemicals which gave rise to the taint may have originated from the board or may have been the result of a chemical reaction in the board during production (probably initiated by the UV light). It has now been confirmed by GC-MS that the conclusions reached by the embodiment of the chemical sensing system according to the invention were in fact correct and that it was the paperboard that was the source of contamination.

Conclusions

This embodiment of the chemical sensing system according to the invention was able to successfully identify a carton as "tainted" which a human sensory panel was unable to detect.

<u>Example 4</u> - The Detection of DIPN in Paperboards Intended for Food Contact

Diisopropylnaphthalenes (DIPNs) have been found in both paperboard and paperboard packaging intended for food contact. It is evident that DIPNs can migrate into the food which they package. The full toxicological effects of DIPNs are currently unknown and manufacturers of paperboard and paperboard packaging have been advised to keep the levels of DIPNs in packaging as low as is practical until such time

that more information is available on the toxicological effects of DIPNs.

Experimental

Six samples of paperboard were analysed using an embodiment of the chemical sensing system according to the invention. 50 x 60 mm squares were cut from the board and no further sample preparation was undertaken. The embodiment of the chemical sensing system according to the invention was used in a method consisting of a 25 second sampling time followed by a 60 second cleaning cycle.

Results

The combined chemical sensor responses to the six samples (which were determined in replicate) were compared using a quantitative data reduction technique. The results are shown in Figure 9.

Discussion

The embodiment of the chemical sensing system according to the invention demonstrated a clear correlation between the combined chemical sensor responses and the concentration of DIPN in the paperboard. The concentration of DIPN was independently verified using a traditional analytical technique. The dynamic range of the embodiment of the chemical sensing system according to the invention with respect to DIPN is wide, ranging from approximately 3mg/kg to in excess of 70 mg/kg. If an allowable limit for DIPN is to be set, it is expected to be in the range of 4 mg/kg. The repeatability of the measurements obtained was

approximately 5%, which is comparable to other methods which have been used to determine DIPN.

CLAIMS

1. A chemical sensing system for analysing the headspace of a sample comprising a modular sampling unit operatively connected to a chemical sensor assembly,
wherein:
(1) said modular sampling unit comprises:
a mount having an inlet channel and an outlet channel for a carrier gas;
a base member having a hollow interior bound by one or more internal side walls and a basal wall, wherein at least a part of the juncture of the basal wall and one or more internal walls is provided with a supporting collar for supporting the whole or part of the edge of the lower face of the sample;
a closure member having one or more exterior side walls and a basal wall defining a body portion, said body portion being complimentarily shaped with the hollow interior of the base member, wherein the outer edge of the basal wall is provided with an upstanding portion capable of engaging the edge of the upper face of the sample,
wherein in use the base member is inserted into the mount and the body portion of the closure member engages the hollow interior of the base member thereby defining a headspace below the lower face of the sample and a headspace above the upper face of the sample such that the inlet channel communicates with the headspace below the lower face of the sample and the outlet channel communicates with the headspace above the upper face of the sample thereby defining a continuous flow path between the inlet and outlet channel across the majority of the surface area of the sample; and
(2) said chemical sensor assembly comprises:

one or more chemical sensors, each chemical sensor having a chemical sensing component capable of exhibiting a measurable and characteristic response to a chemical stimulus;

a solid body having an entry end for admitting a carrier gas, an exit end for exhausting a carrier gas and one or more compartments for housing each of the one or more chemical sensors therebetween, said one or more compartments being in consecutive fluid communication so as to define a continuous flow path between the entry end and the exit end of the solid body in which the chemical sensing component of the or each chemical sensor may be exposed to the carrier gas.

2. A system as claimed in claim 1 wherein the inlet channel is connected to the headspace below the lower face of the sample by a basal conduit in the basal wall of the base member.

3. A system as claimed in claim 1 or 2 wherein the outlet channel is connected to the headspace above the upper face of the sample by a side conduit in the side wall of the base member.

4. A system as claimed in claim 3 wherein the headspace above the upper face of the sample and the side conduit are connected in fluid communication by a linear tube disposed radially in the upstanding portion of the closure member.

5. A system as claimed in any preceding claim wherein the headspace below the lower face of the sample is in fluid communication with the headspace above the upper face of the sample via one or more substantially U-shaped tubes.

6. A system as claimed in claim 5 wherein a first arm of the U-shaped tube is disposed radially in the supporting collar of the base member and a second arm of the U-shaped tube is disposed radially in the upstanding portion of the closure member, the first and second arm being connected in fluid communication by a connecting portion in the side wall of the base member.

7. A system as claimed in any preceding claim wherein the basal wall of the base member comprises a protrusion for supporting the lower face of the sample.

8. A system as claimed in claim 7 wherein the protrusion converges to a reduced contact end.

9. A system as claimed in any preceding claim wherein the body portion of the closure member is threadedly engaged within the hollow interior of the base member.

10. A system as claimed in any preceding claim wherein the base member is a tight push fit into the mount.

11. A system as claimed in any preceding claim wherein the exterior face of the basal wall of the base member and the mount comprise a locating arrangement to enable correct positioning and insertion of the base member in the mount.

12. A system as claimed in any preceding claim wherein each compartment of the solid body is arranged such that the chemical sensing component is exposed to the carrier gas in a wall jet fashion.

13. A system as claimed in any preceding claim wherein the entry end for admitting a carrier gas and the exit end for exhausting a carrier gas are connected by a substantially linear conduit.

14. A system as claimed in claim 13 wherein the substantially linear conduit defines a spine connecting each of the compartments consecutively.

15. A system as claimed in any preceding claim wherein each compartment is adapted to house the chemical sensing component in substantially free space.

16. A system as claimed in any preceding claim wherein the chemical sensor assembly comprises a plurality of chemical sensors.

17. A system as claimed in any preceding claim wherein the or each chemical sensor is a quartz crystal chemical sensor.

18. A chemical sensor assembly as defined in any of claims 1 to 17.

19. A modular sampling unit as defined in any of claims 1 to 17.

20. A method for detecting the presence of one or more chemical stimuli in the headspace of food packaging material using a chemical sensing system as defined in any of claims 1 to 17, said method comprising:

inserting the base member into the mount;

positioning a sample of the food packaging material in the hollow interior of the base member such that the sample is supported on the supporting collar;

engaging the body portion of the closure member with the hollow interior of the base member;

sweeping the headspace of the sample with a carrier gas;

passing the carrier gas containing one or more chemical stimuli from the headspace to the entry end of the chemical sensor assembly;

measuring the response of the chemical sensors to the carrier gas containing the one or more chemical stimuli from the headspace; and

relating the response to the presence of the one or more chemical stimuli.

21. A method as claimed in claim 20 wherein the chemical stimulus of interest is a DIPN.

22. A method as claimed in claim 20 wherein the chemical stimulus of interest is hexanal.

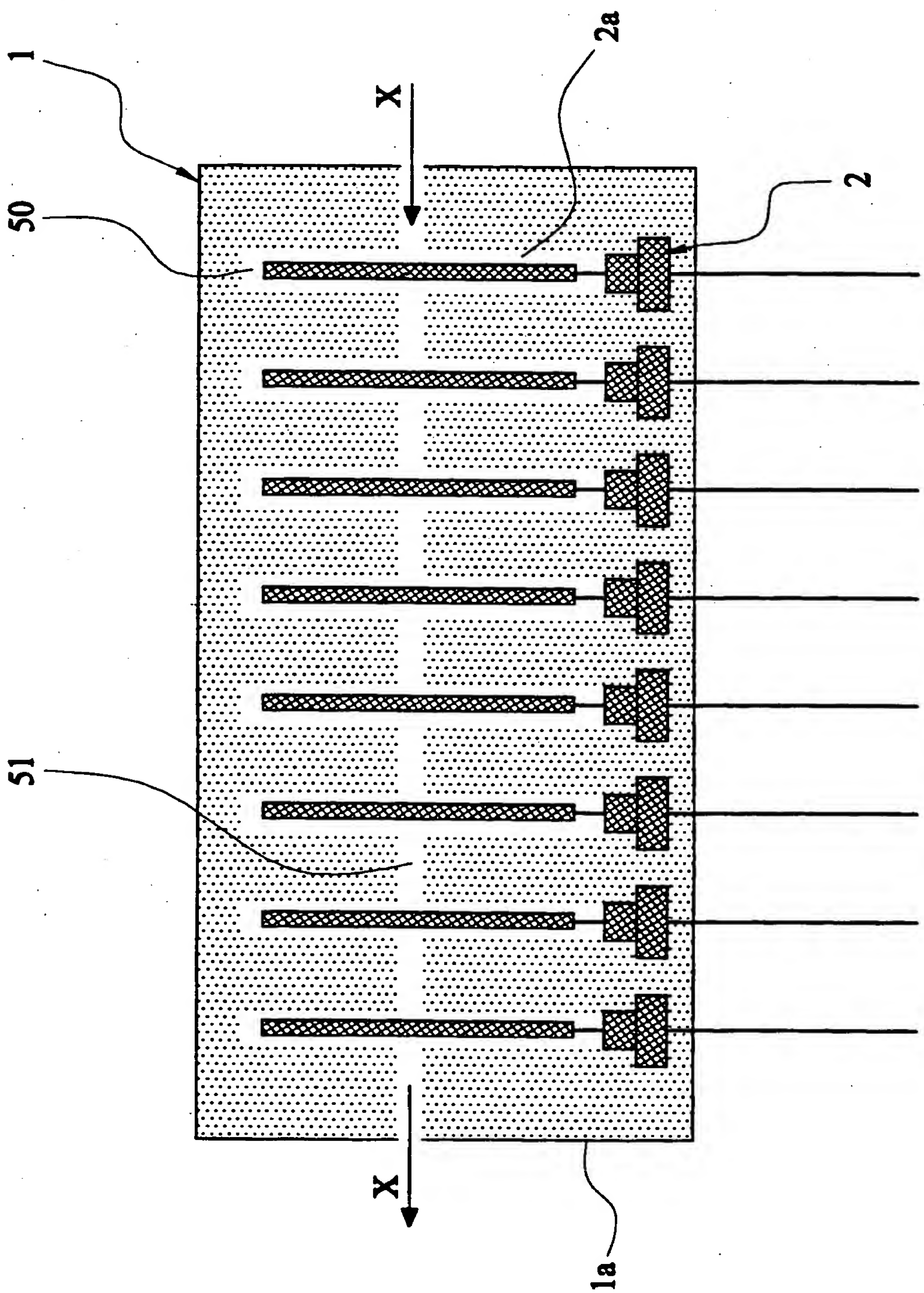


FIG. 1

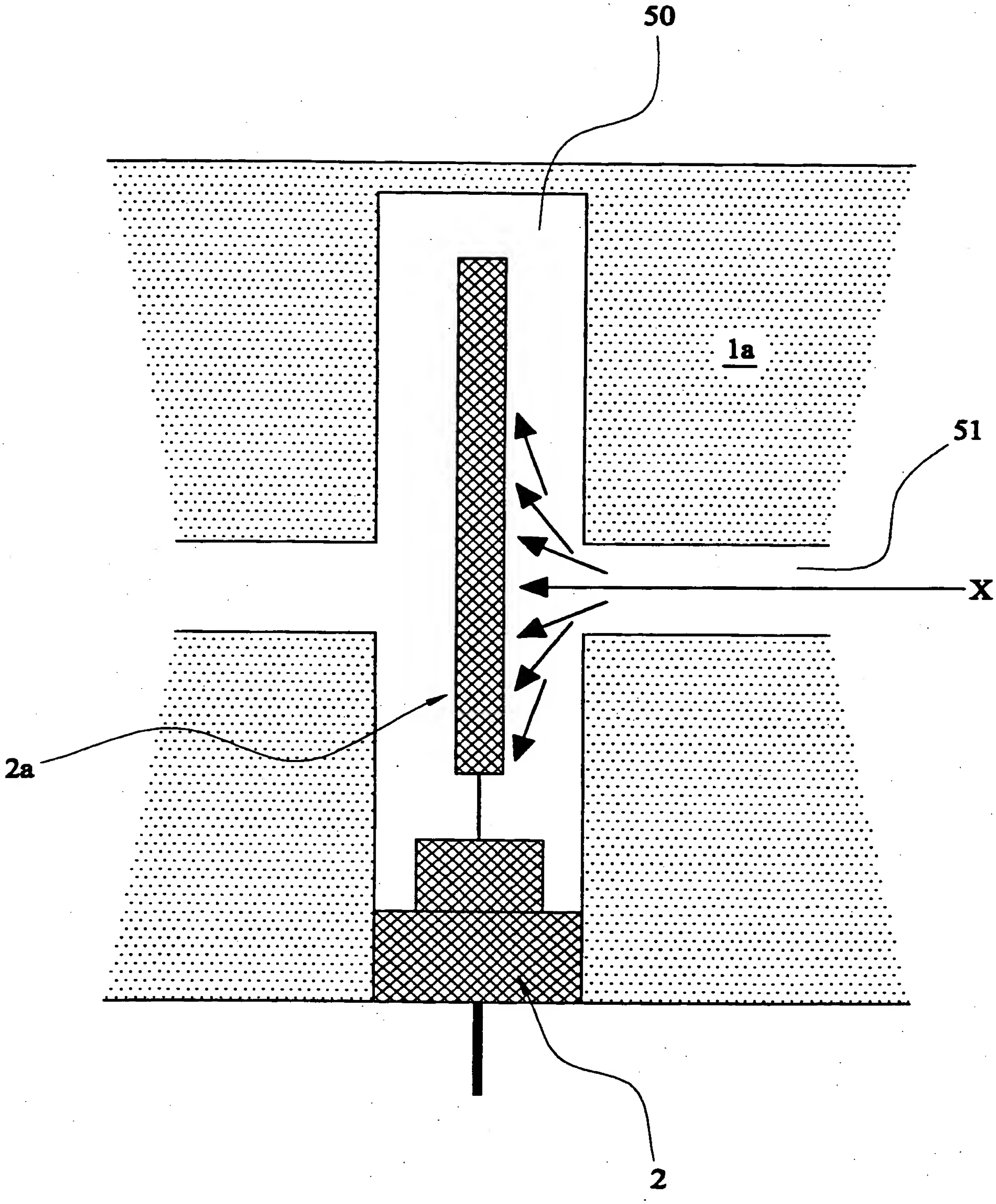


FIG. 2

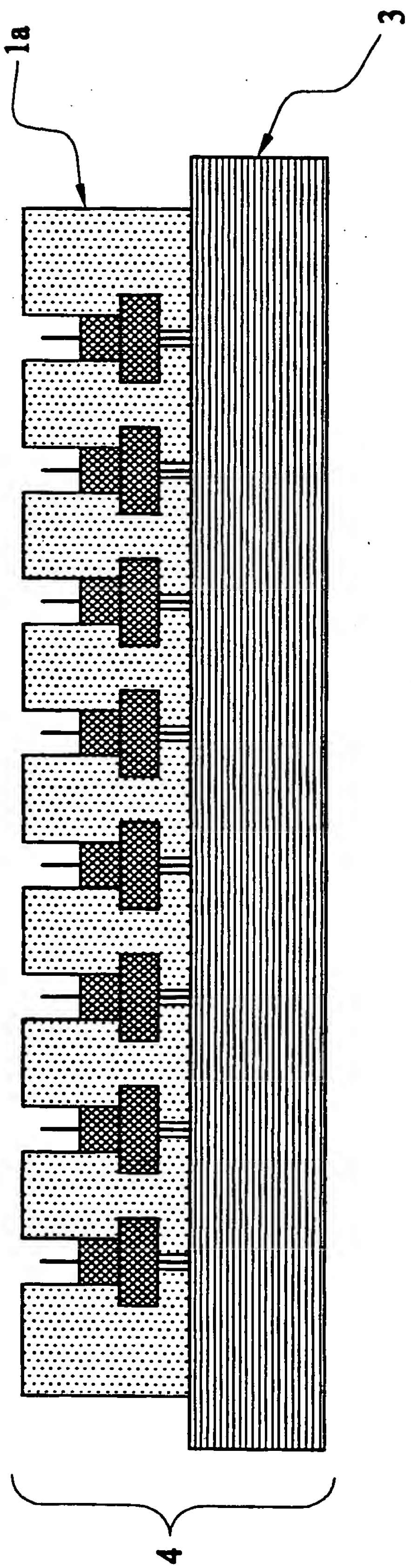


FIG. 3

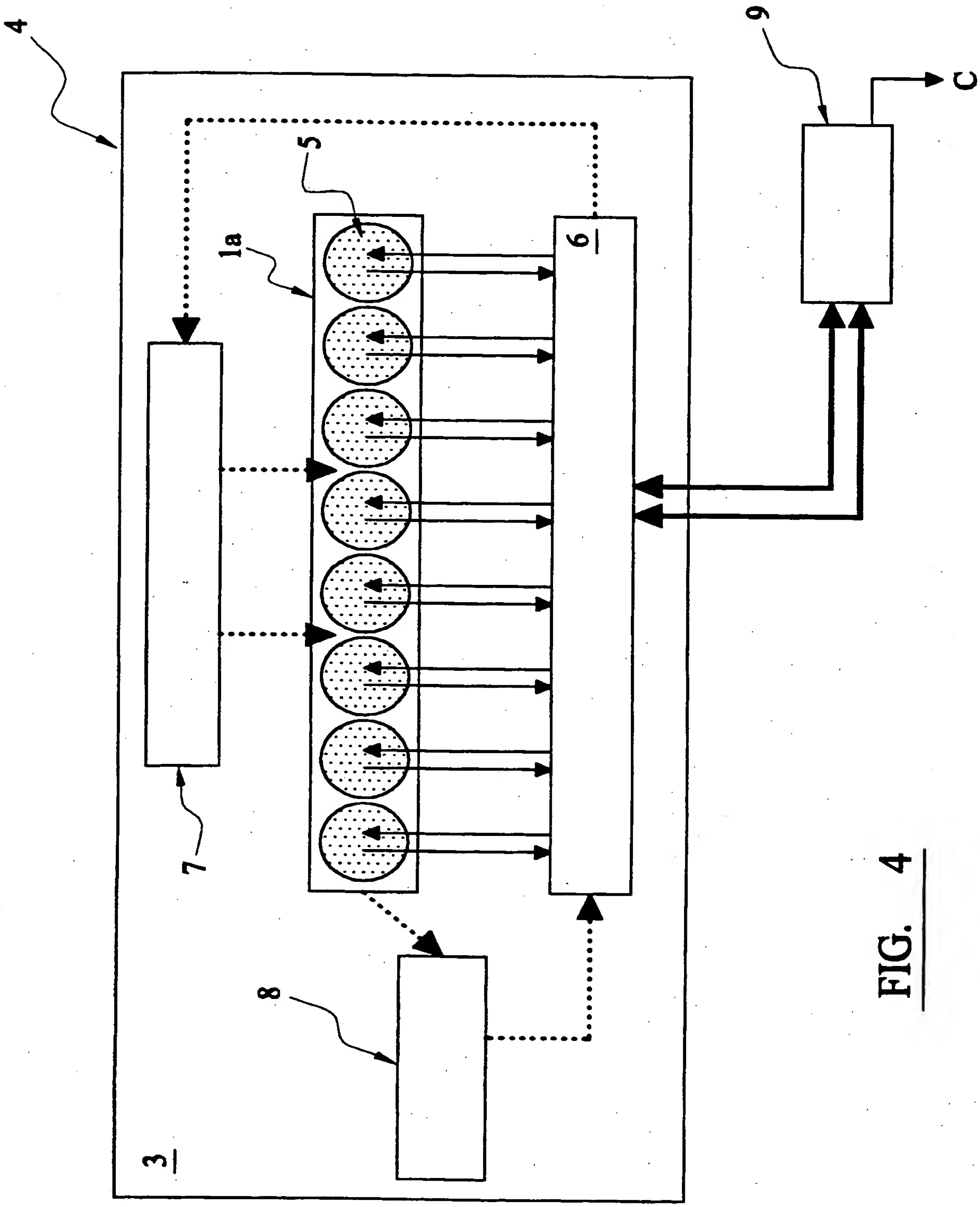


FIG. 4

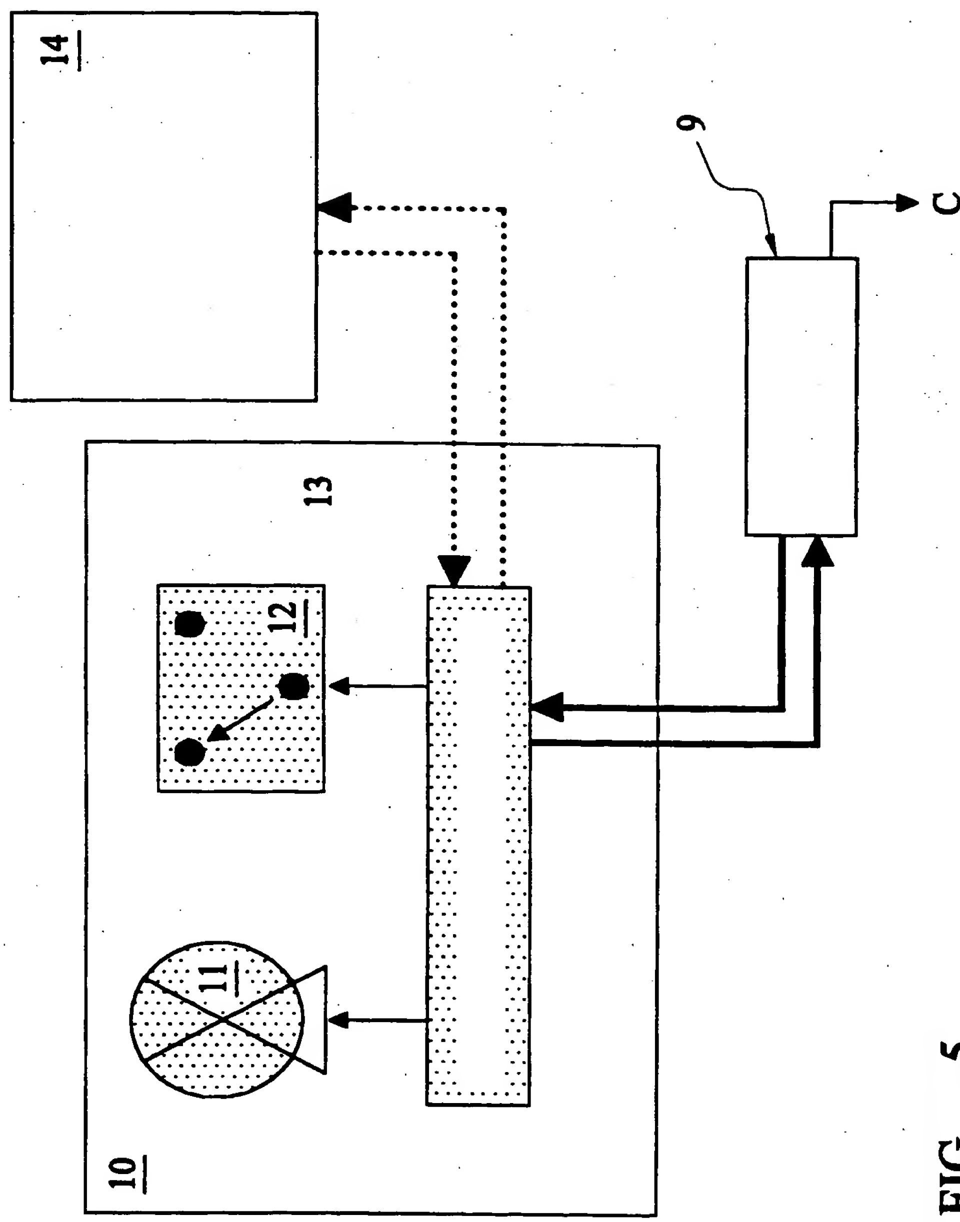


FIG. 5

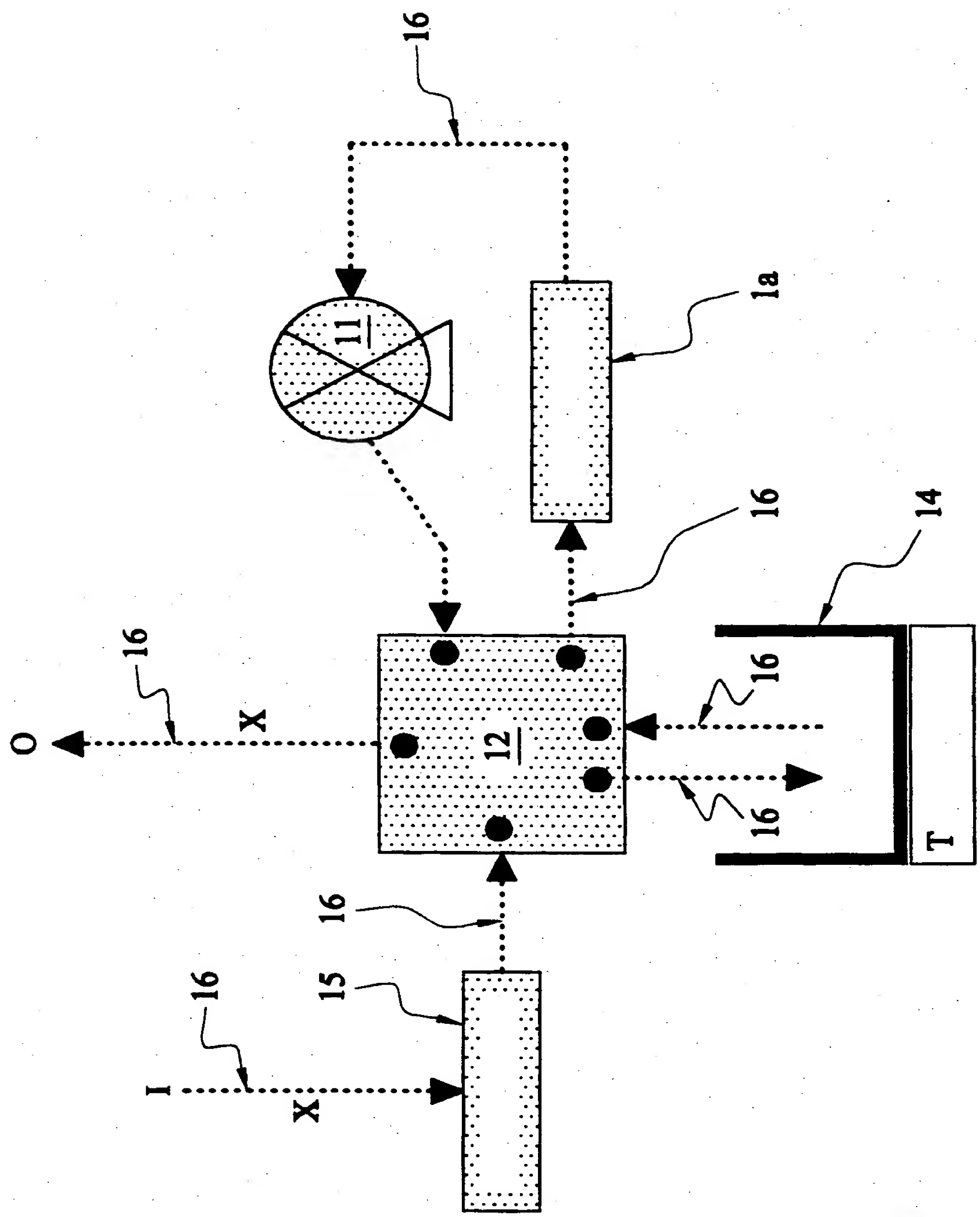


FIG. 6

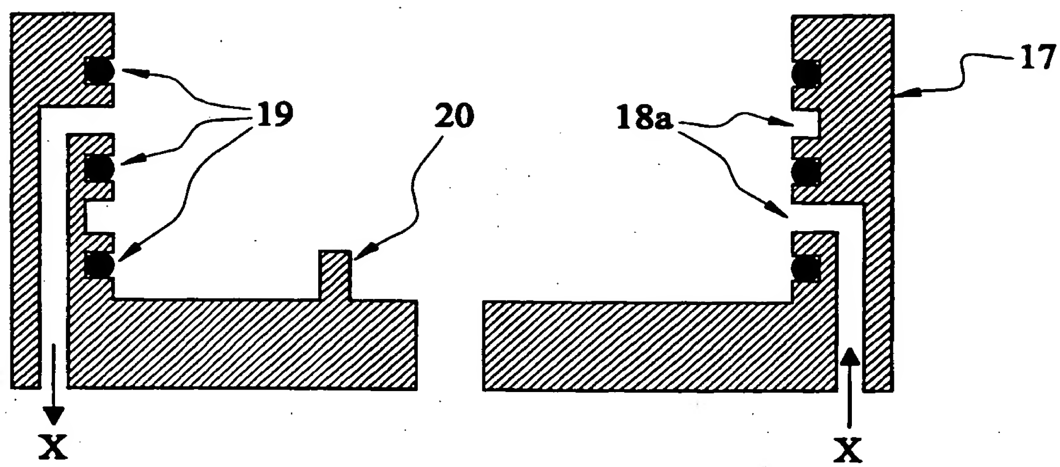


FIG. 7a

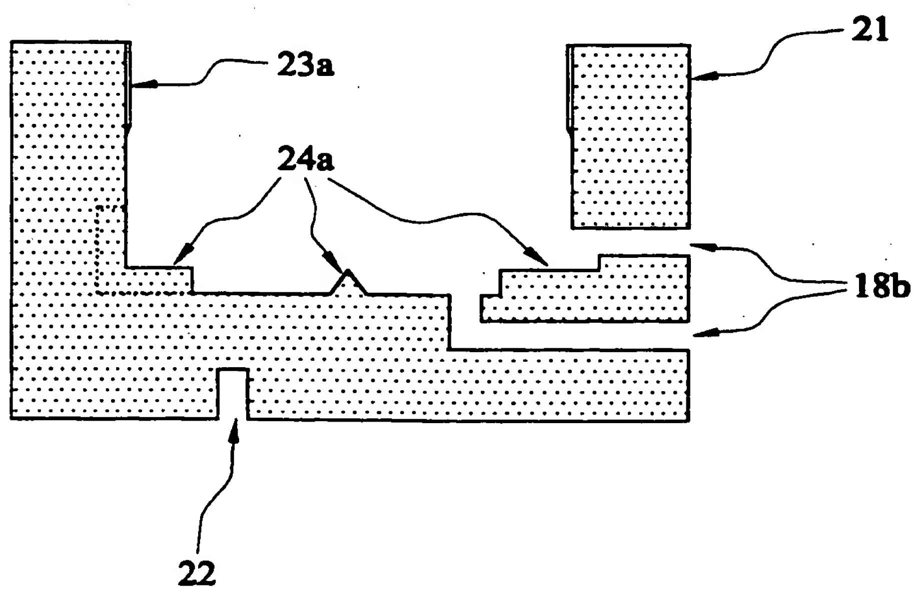


FIG. 7b

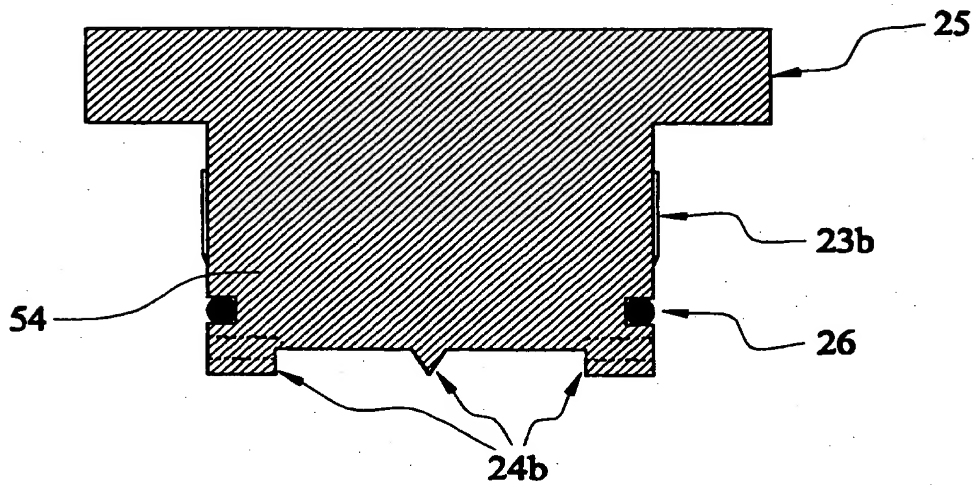


FIG. 7c

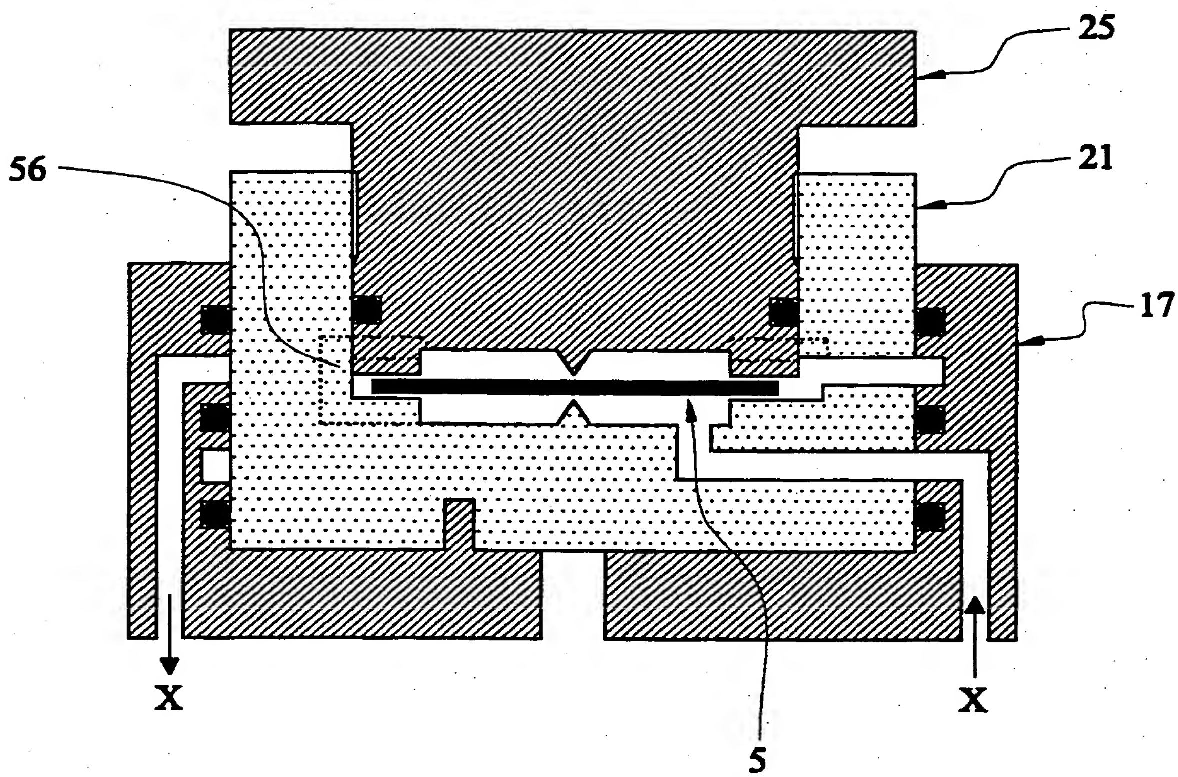


FIG. 7d

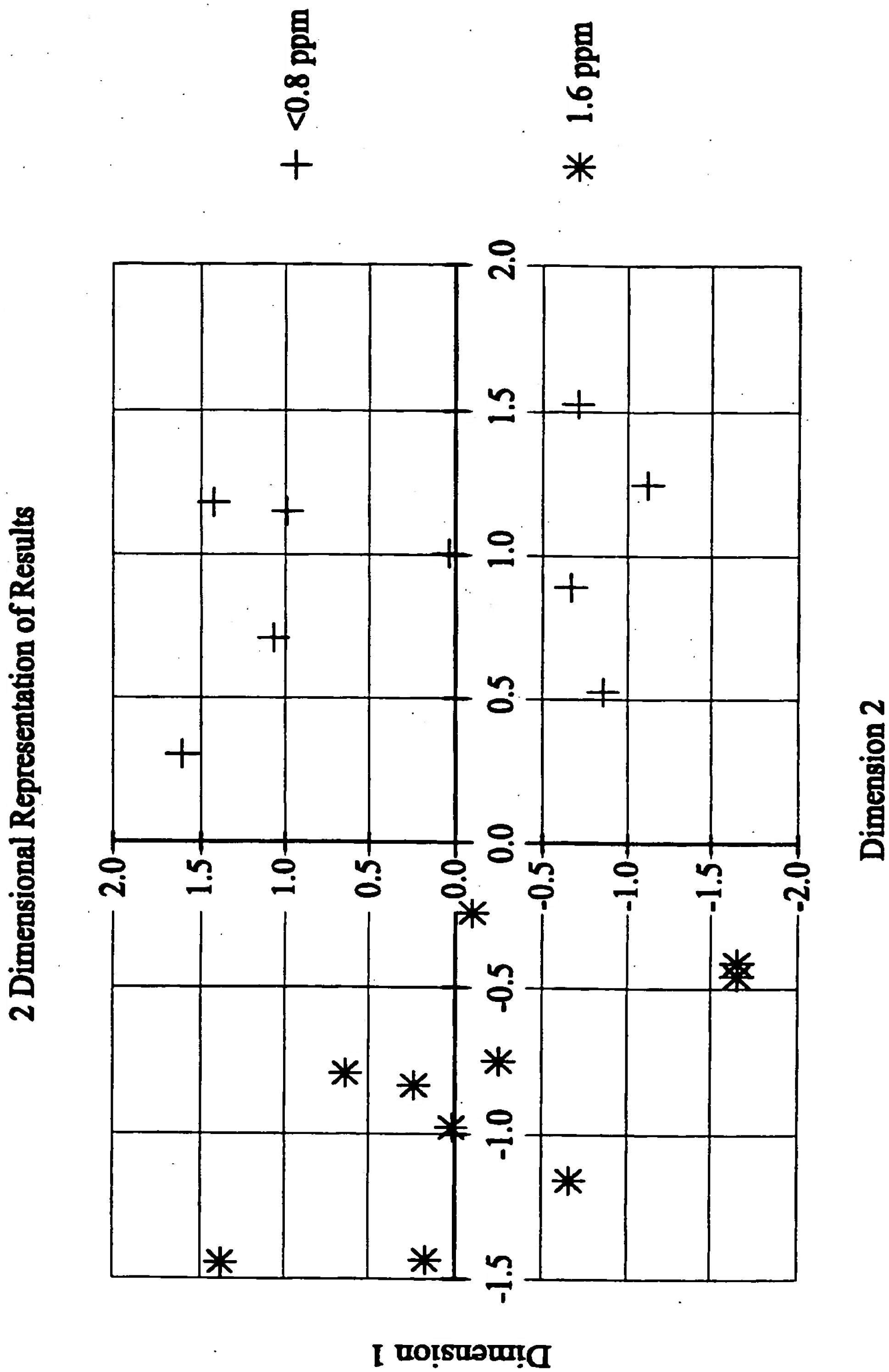

2 Dimensional Representation of Results
+ <0.8 ppm
✳ 1.6 ppm
Dimension 1
Dimension 2
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

FIG. 8

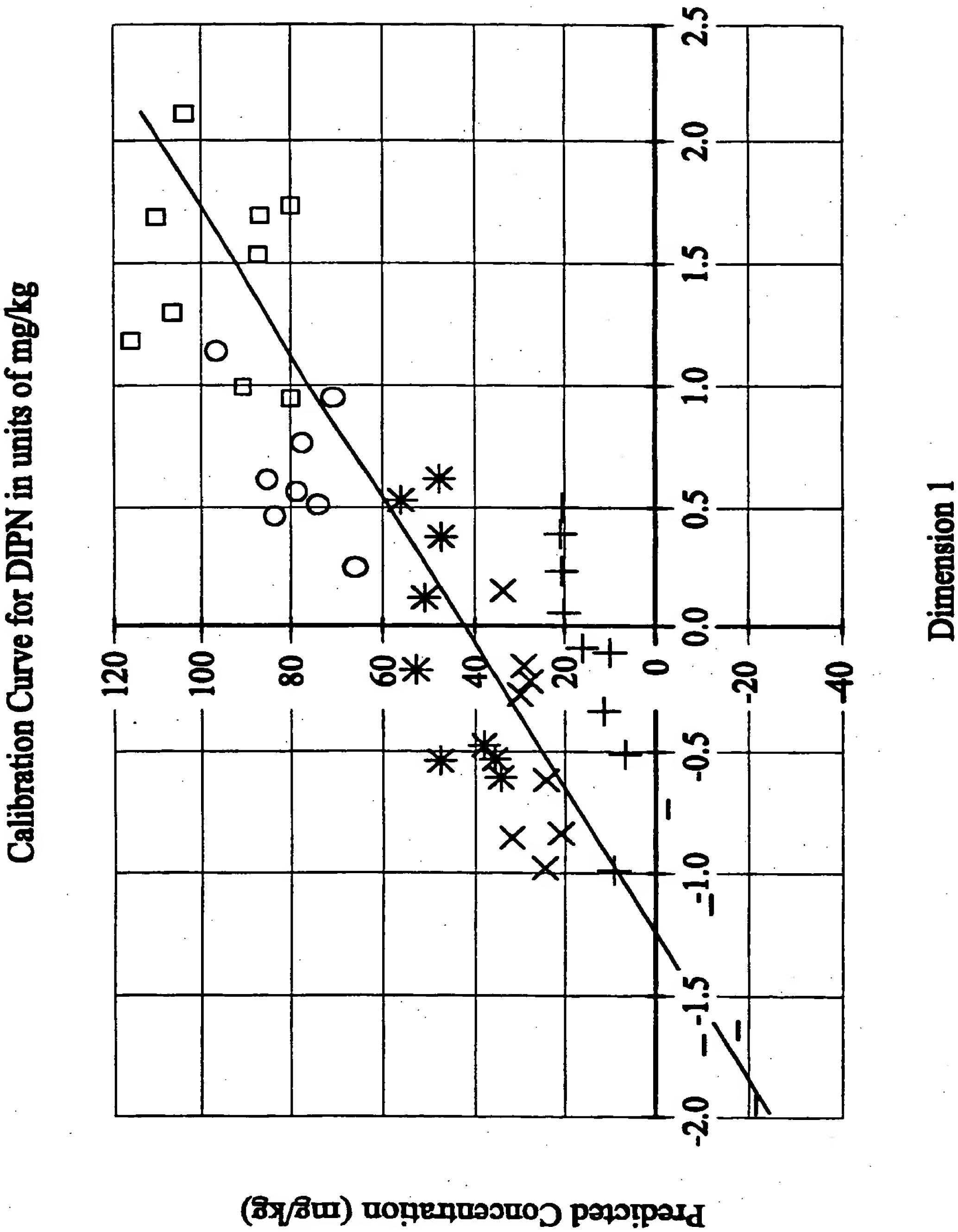

Calibration Curve for DIPN in units of mg/kg
Predicted Concentration (mg/kg)
Dimension 1
120
100
80
60
40
20
0
-20
-40
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5

FIG. 9

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 00/03664

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N33/00 G01N33/34 G01N1/00 G01N33/02 G01N33/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 567 782 A (HEWLETT PACKARD CO) 3 November 1993 (1993-11-03) column 1, line 8 -column 2, line 29; figure 1 column 3, line 25 -column 4, line 10 column 6, line 41 -column 7, line 32	1,20
A	US 5 482 524 A (NAKANO KAZUO ET AL) 9 January 1996 (1996-01-09) column 2, line 14 - line 35 column 5, line 11 - line 57; figure 1	1,20
A	US 5 469 369 A (ROSE-PEHRSSON SUSAN L ET AL) 21 November 1995 (1995-11-21) column 3, line 48 - line 60 column 4, line 37 - line 66 column 8, line 35 - line 50 column 11, line 59 - line 65	17

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 March 2001	07/03/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Joyce, D

3

International Application No
PCT/GB 00/03664

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 184 037 A (FURNITURE IND RES ASS) 17 June 1987 (1987-06-17) page 1, column 1, line 7 -page 1, column 2, line 122	1,20
A	OGURI N ET AL: "DEVELOPMENT OF A CURIE-POINT HEADSPACE SAMPLER FOR CAPILLARY GAS CHROMATOGRAPHY" JOURNAL OF HIGH RESOLUTION CHROMATOGRAPHY,WILEY VCH, WEINHEIM,DE, vol. 14, no. 2, February 1991 (1991-02), pages 79-82, XP000200269 ISSN: 0935-6304 the whole document	1
A	WO 97 46755 A (AXRUP LARS ;NILSSON TORSTEN (SE); KORSNAES AB PUBL (SE)) 11 December 1997 (1997-12-11) page 1, line 26 -page 3, line 19	22

3

INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No
PCT/GB 00/03664

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0567782	A	03-11-1993	US	5363707 A	15-11-1994
			JP	6043075 A	18-02-1994
US 5482524	A	09-01-1996	JP	7083808 A	31-03-1995
US 5469369	A	21-11-1995	NONE		
GB 2184037	A	17-06-1987	NONE		
WO 9746755	A	11-12-1997	SE	504875 C	20-05-1997
			AU	3113597 A	05-01-1998
			CA	2257215 A	11-12-1997
			EP	0907789 A	14-04-1999
			SE	9602225 A	20-05-1997

THIS PAGE BLANK (USPTO)